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MIST FLAMMABILITY STUDIES
OF CANDIDATE FIRE-RESISTANT
HYDRAULIC FLUIDS

S. G. PANDE
GEO-CENTERS, INC.

J. B. ROMANS
R. C. LITTLE

NAVAL RESEARCH LABORATORY
N00014-83-C-2274
PREPARED FOR

U.S. NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVENUE, S. W.
WASHINGTON, D. C. 20375

PREPARED BY
GEO-CENTERS, INC.
320 NEEDHAM STREET
NEWTON UPPER FALLS, MA 02164

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ABSTRACT

Using NRL's mist flammability test apparatus, several commercial samples of 40% water-in-oil emulsions (fire-resistant hydraulic fluids) were screened for fire resistancy.* For comparison purposes, two other commercial fire-resistant hydraulic fluids were screened viz., a water-glycol solution and a phosphate ester. The Navy's currently used petroleum-type hydraulic fluid, 2190-TEP, was employed as the reference fluid.

At the most severe conditions investigated (i.e., spray disk tangential velocity of 67.8 m/s, and fluid flow rate of 850 ml/min), none of the fire-resistant hydraulic fluids exhibited ignition leading to propagation in the presence of the propane test flame, indicating fire resistancy under these conditions. Under identical operating conditions, 2190-TEP exhibited gross ignition with propagation of flame ranging from 180° to 360° around the spinning disk, indicating it to be a potential fire hazard. The physical and chemical characteristics of the 40% water-in-oil emulsions suggest that this class of fire-resistant hydraulic fluids may be suitable replacement candidates for 2190-TEP. These promising results therefore warrant further study.

* (The term 'fire-resistancy' relates to specific flammability test conditions.)

1. INTRODUCTION

Mist flammability of petroleum fluids leading to catastrophic fires and explosions is well known [1-2]. Because of the cost in lives and equipment, the phenomenon of mist flammability is of serious concern to the success of both civilian and military operations. In military operations for example, the petroleum oil, MIL-L-17331 (2190-TEP), currently used in the U.S. Navy's submarine high pressure hydraulic systems, poses a potential explosion and fire hazard in the event of fluid spray leakage. Such a situation can arise by lines fracturing under stress, induced, for example by accident, enemy attack, or perhaps simply old age. Ignition of the fine mist of petroleum fluid (not hazardous in bulk form) would subsequently gravely endanger the lives of the crew and the accomplishments of the mission.

Efforts to minimize or eliminate such potentially fire hazardous situations have focused on the development of fire-resistant hydraulic fluids [2-6]. The development of adequate fire-suppressive agents for hydraulic fluids has been less successful [7]. Commercially available fire-resistant hydraulic fluids can be classified into two major categories: Water-containing fluids and water-free fluids. Water-containing fluids derive their fire-resistant properties from their water content [1,2,7-9] and include emulsions which contain ~40% to 95% water and water-glycol solutions which contain ~40% water. Water-free fluids, on the other hand, derive their fire-resistant properties from their molecular structure [2,9] and include the synthetic fluids viz., phosphate esters, organo phosphates, silicate esters, silicones and halocarbons. The physical and chemical characteristics of the 40% water-oil emulsions (also referred to as invert emulsions) suggest that this class of fire-resistant hydraulic fluids may contain suitable replacement candidates for 2190-TEP

hydraulic oil. For example, the invert emulsions exhibit the following advantages over other fire-resistant fluids [1,2,5]: good lubricity and resistance to leakage, compatibility with the majority of seals and hoses, superior metal compatibility, minimum effect on paints, lower cost relative to the water-glycol solutions and the synthetic fluids, and are relatively safe. More in depth information on water-base and water-free fire-resistant fluids may be found in Hatton [3b].

In this report, five invert emulsions from four different manufacturers were screened for fire-resistancy, using the NRL mist flammability test apparatus [7]. For comparison purposes, two other types of commercial fire-resistant hydraulic fluids were also screened viz., a glycol-water solution and a phosphate ester. The Navy's petroleum-type hydraulic fluid 2190-TEP was employed as the reference fluid.

2. EXPERIMENTAL

2.1 Materials

The eight hydraulic fluids covered in this report and their suppliers are as follows:

(1) Invert Emulsions:

- (a) Sunsafe 450 (SS 450)* Sun Petroleum Products Co., Philadelphia, PA.
- (b) Mobil Pyrogard D (Mobil Pyg D)*, Mobil Technical Services Laboratory, Princeton, NJ.
- (c) Houghto-Safe 5046 (HTO Safe 5046)* and Houghto-Safe 5047 F (HTO Safe 5047 F)*, E.F. Houghton and Co., Valley Forge, PA.
- (d) Quintolubric 958-30 (Q-Lubric 958-30)* Quaker Chemical Corporation, Conshohocken, PA.

(2) Water-Glycol Solution:

Houghto-Safe 273 (HTO Safe 273)* E.F. Houghton and Co., Valley Forge, PA.

(3) Phosphate Ester:

Houghto-Safe 1120 (HTO Safe 1120)* E.F. Houghton and Co., Valley Forge, PA.

(4) Petroleum-type hydraulic fluid:

2190-TEP, Military Specification (MIL-L-17331F Ships 1973 General Services Administration (GSA), Washington, DC.

* Abbreviation used in this report.

The fire-resistant hydraulic fluids were used as received from the manufacturer or supplier, except for initial stirring prior to testing. A list of some of the pertinent properties of the hydraulic fluids screened, as specified by the manufacturer or military specifications, is given in Table I.

2.2 Apparatus

A schematic diagram of the flammability apparatus, which has been used at this laboratory with both aviation jet aircraft fuels and hydraulic fluids, is shown in Figure 1. A motorized syringe delivers the fluid to the center of an electrically driven spinning disk atomizer patterned after the one used by Mannheimer [11] with aviation jet aircraft fuel compositions. The spinning disk (4.25 inches diameter) dispenses the fluid into the atmosphere as a mist. The low pressure spinning disk atomizer has the advantage that the flammability of the mists produced is a function of disk speed [7,11,12]. Rotational speed of the disk is variable and is measured by a Digistrobe Stroboscope-Tachometer. A propane burner, located eight inches from the center of the spinning disk, serves as the ignition source. At this burner location, the mist from the disk forms a spray band about three inches in height within the speed range of 10,000 to 12,000 rpm (56.6 to 67.8 m/s tangential velocity). In previous work with the flammability apparatus [7,11,12], the top of the burner barrel had been located 0.5 inch below the top surface of the disk. This placed the hottest portion of the test flame in the upper region of the spray band which presumably contained the smallest size droplets and was therefore the most flammable portion of the spray band. Since the top of the burner barrel occupied a position in the lower portion of the spray band a secondary source of ignition may have resulted from drop vaporization effects. Some of the fire-resistant fluids were studied at the 0.5 inch burner elevation. In order to minimize the hot surface effect, the remaining hydraulic fluids were studied with the burner lowered 1.50 and

TABLE I - Properties of Hydraulic Fluids Screened

| Hydraulic Fluid | Flash Point ^a °C | Pour Point ^b °C | Water Content ^c % | pH (Neutralization Number) ^d | Viscosity ^e at 37.8°C CS | Rust Protection ^f | Corrosion Resistance ^g |
|-----------------------------------|--------------------------------|-------------------------------|---------------------------------|---|---|------------------------------|--|
| Invert Emulsions: SS 450 | Not Applicable | -34.4 | 40 | 7.9 | 97h | Pass ¹ | Yes |
| Mobil Pyg D | " | -29 | 41c+j | 9.5k | 117.6e+l | Pass | " |
| HFO-Safe 5046 | " | -18 | 40 | 9.0(.84) | 88.5 | Pass | " |
| HFO-Safe 5047-pm | " | -18 | 40 | 9.0(.84) | 88.5 | Pass | " |
| Q-Lubric 958-30 | " | -23.3 | 46 | 8 to 8.5 | 64.7 | Pass | " |
| Water-Glycol: HFO-Safe 273 | " | -39 | 45 | 9.4 | 44 | Pass | but incompatible with Zn, Cd, Mg unanodized Al |
| Phosphate Ester: HFO-Safe 1120 | 236(1538)°C | -20.6 | .1 | (.1) | 49.5 | Pass | Yes ^p |
| Petroleum: 2190-TBP | 204.4 min. | -6.7 max | None | Neutral, (.3)max | 82-110 ^l | Pass | Yes |

- a. ASTM Method D92
 b. ASTM Method D92
 c. ASTM Method D95
 d. ASTM Method D974
 e. ASTM Method D88
 f. ASTM Method D665A - Rust protection, fresh water
 g. Specific to metals normally found in hydraulic systems - manufacturer's data; slight tarnish to copper permitted. ASTM Method D-130
 h. ASTM Method D2161
 i. ASTM Method D665B - Rust protection, synthetic sea water
 j. ASTM Method D1744
 k. Method ARD 1167
 l. ASTM Method D445
 m. Differs from HFO-Safe 5046 only in corrosion resistant properties
 n. MIL-H-22072B requirements
 o. ASTM Method D-2155
 p. MIL-H-19457B (Ships) Type 1 specification

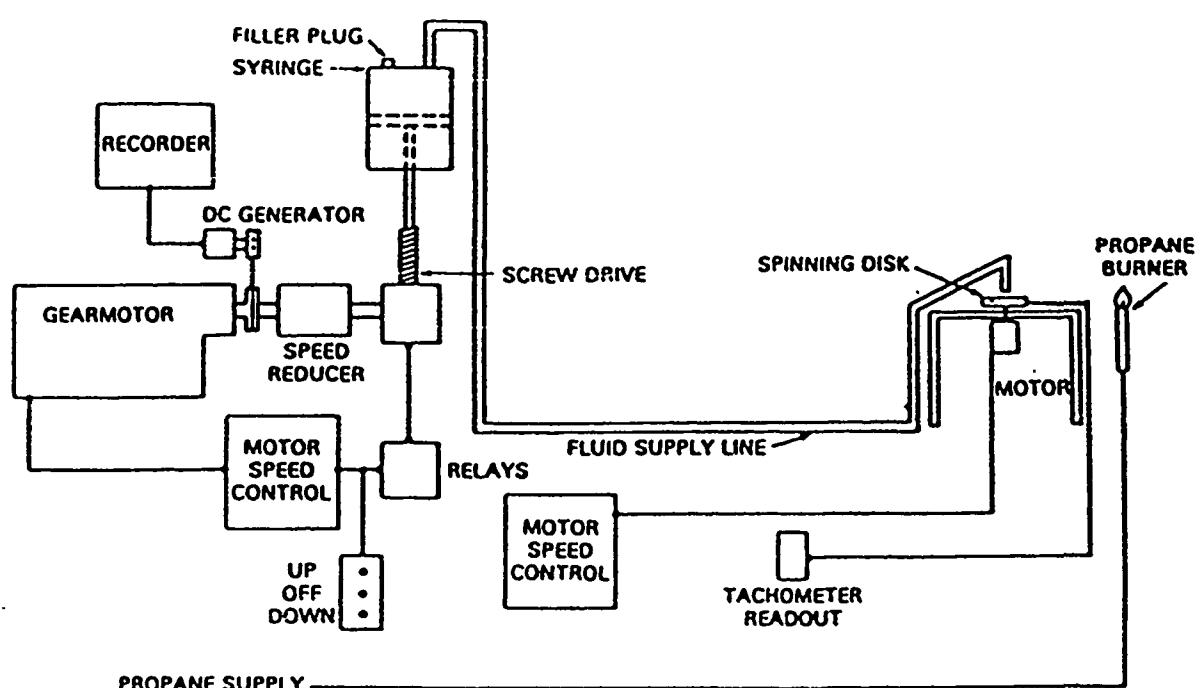


Fig. 1 — Schematic diagram of NRL flammability apparatus

1.75 inches below the top of the disk. Because of frequent extinguishment of the test flame by the phosphate ester, some trials of this material were conducted with the burner lowered an additional inch to 2.75 inches below the top of the disk.

Flammability characteristics, viz. ignition of the fluid mist and propagation of the flame, were detected visually and photographed; the relative flame intensity was measured with a photocell (not shown in Figure 1) and recorded on a dual-pen strip-chart recorder. Additional details of the flammability apparatus have been described in previous reports [7,11].

2.3 Procedure

In earlier mist flammability studies [7], most of the fluids screened (especially those containing carbon), tended to cause the blue propane test flame to become luminous as mist from the spinning disk passed through the flame. In this report, the criterion for fire resistancy was the absence of "ignition leading to propagation" of yellow flame away from the test flame.

Previous work had also shown that increasing the disk speed resulted in decreasing mist droplet size [11] and that the severity of the test increased with disk speed [10-12). The fluids under study were monitored for ignition and propagation as a function of initial disk speed. The test involved a decreasing series of disk speeds for each fluid. The procedure was the same as that described in a previous report [12] for evaluating the mist flammability of jet fuel formulations. Specifically, it involved an initial disk speed of 12,000 rpm which was decreased at 1000 rpm intervals until no further effect of disk speed reduction was observed. Where applicable, each test was then repeated in a similar manner but with an initial disk speed of 11,500 rpm. The tests were performed at two rates of fluid delivery to the spinning disk, viz. 400 ml/minute and 850 ml/minute.

Care was taken to avoid mixing a candidate fluid with the fluid used during the previous flammability test. Generally, the cleaning procedure consisted of purging the delivery system with compressed air, followed by filling the syringe with an appropriate solvent or solvent mixture, pumping the mixture out and purging the system with compressed air. This was repeated two or three times, depending on the nature of the fluid being removed. JP-5 aviation jet aircraft fuel and heptane were used to remove 2190-TEP hydraulic oil. JP-5 and isopropyl alcohol and/or acetone and heptane were used to remove the other fluids studied. The syringe was then filled with the test fluid, and the system pumped out and purged with compressed air. This was repeated twice. The syringe was filled a fourth time and the fluid pumped out without purging before finally recharging the syringe.

3. RESULTS AND DISCUSSION

3.1 RESULTS

3.1.1 Fire Resistant Hydraulic Fluids

Results of the mist flammability tests of the fire-resistant hydraulic fluids are summarized in Table II. As alluded to in the Experimental Section, mist flammability was investigated at various burner heights. Also, as mentioned earlier, Houghto-Safe 1120 phosphate ester was studied with the burner at the lowest level (2.75") because this fluid frequently extinguished the test flame at the higher burner position. As seen from Table II, under severe conditions of the test, (12,000 rpm disk speed and a fluid delivery rate of 850 ml/min), none of the fire-resistant fluids exhibited ignition leading to propagation of flame away from the test flame. Tests were not run at disk speeds less than 10,000 rpm since no significant differences in results occurred within the 12,000-10,000 rpm range. All the fire-resistant fluids caused the test flame to become luminous and no significant differences in fire resistancy were observed among them: Figure 2 is typical of the behavior of the invert fluids. However a slight growth in test flame size was observed with HTO-Safe 5047 F. Luminosity of the test flame was least with the water-glycol fluid (Figure 3) and greatest with the phosphate ester which also caused test flame growth during some of the ignition trials (Figure 4).

Even though the test flame became luminous during the tests, the intensity of the light from the burner was only slightly greater than that of ambient lighting of the test apparatus required to obtain satisfactory photographs. Consequently the response of the photocell was minimal, amounting to no more than 1 mv even during testing of the phosphate ester fluid.

Table II - Mist Flammability of Fire-Resistant Fluids

| Fluid | Burner Position* (inch) | Fluid Delivery Rate, ml/min | Ignition with Flame Propagation** |
|--|-------------------------|-----------------------------|-----------------------------------|
| SS 450 | 0.5 | 400 | No |
| | " | 850 | No |
| Mobil Pyg D | 0.5 | 400 | No |
| | " | 850 | No |
| HTO-Safe 5046 | 0.5 | 400 | No |
| | " | 850 | No |
| HTO-Safe 273 | 0.5 | 400 | No |
| | " | 850 | No |
| HTO-Safe 5046 | 1.75 | 400 | No |
| | " | 850 | No |
| HTO-Safe 5047F | 1.75 | 400 | No |
| | " | 850 | No |
| Q-Lubric 958-30 | 1.75 | 400 | No |
| | " | 850 | No |
| HTO-Safe 1120 | 1.75 | 400 | No |
| | " | 850 | No |
| HTO-Safe 1120 | 2.75 | 400 | No |
| | " | 850 | No |
| * Below top of spinning disk. ** At spray disk speed of 12,000 rpm. | | | |

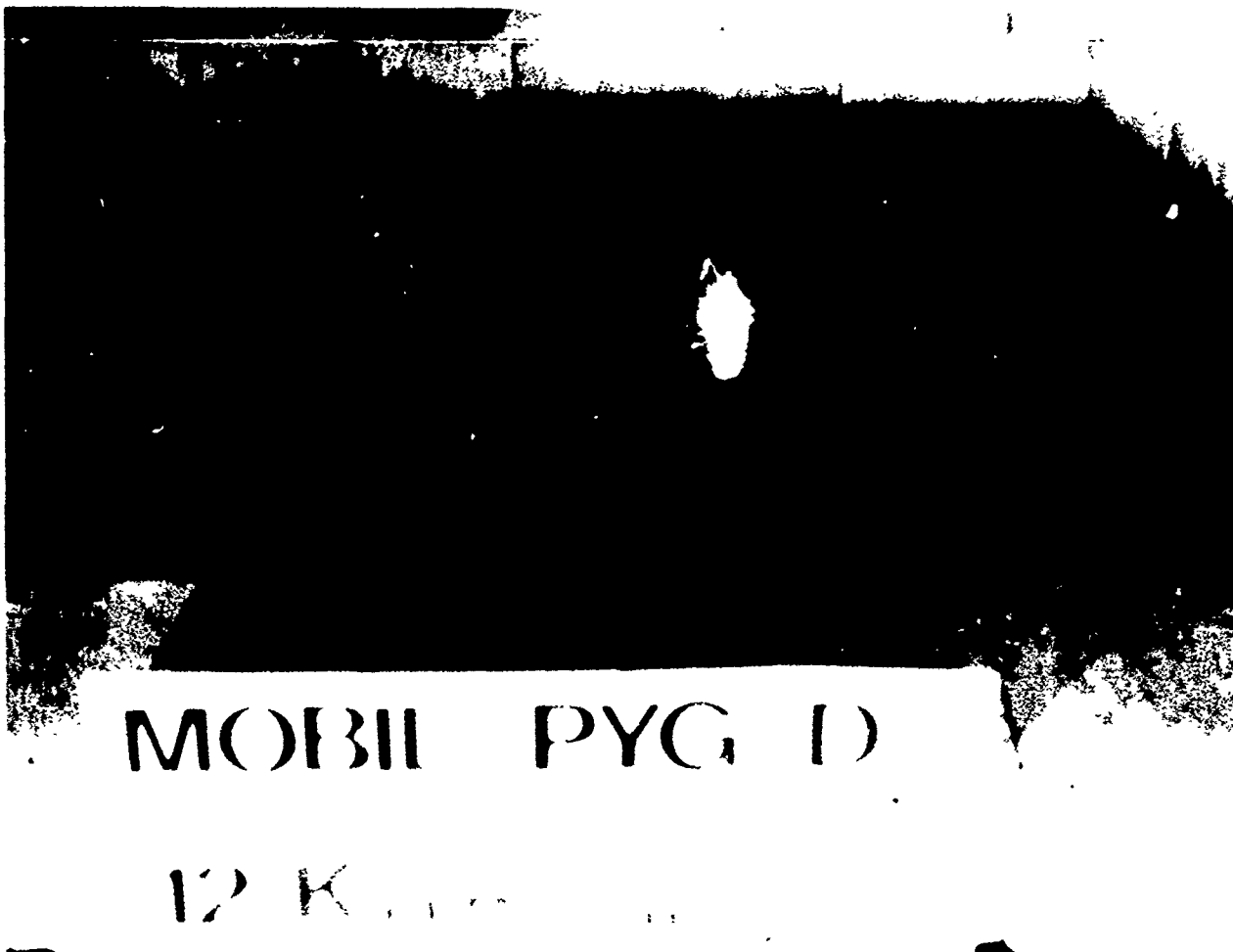
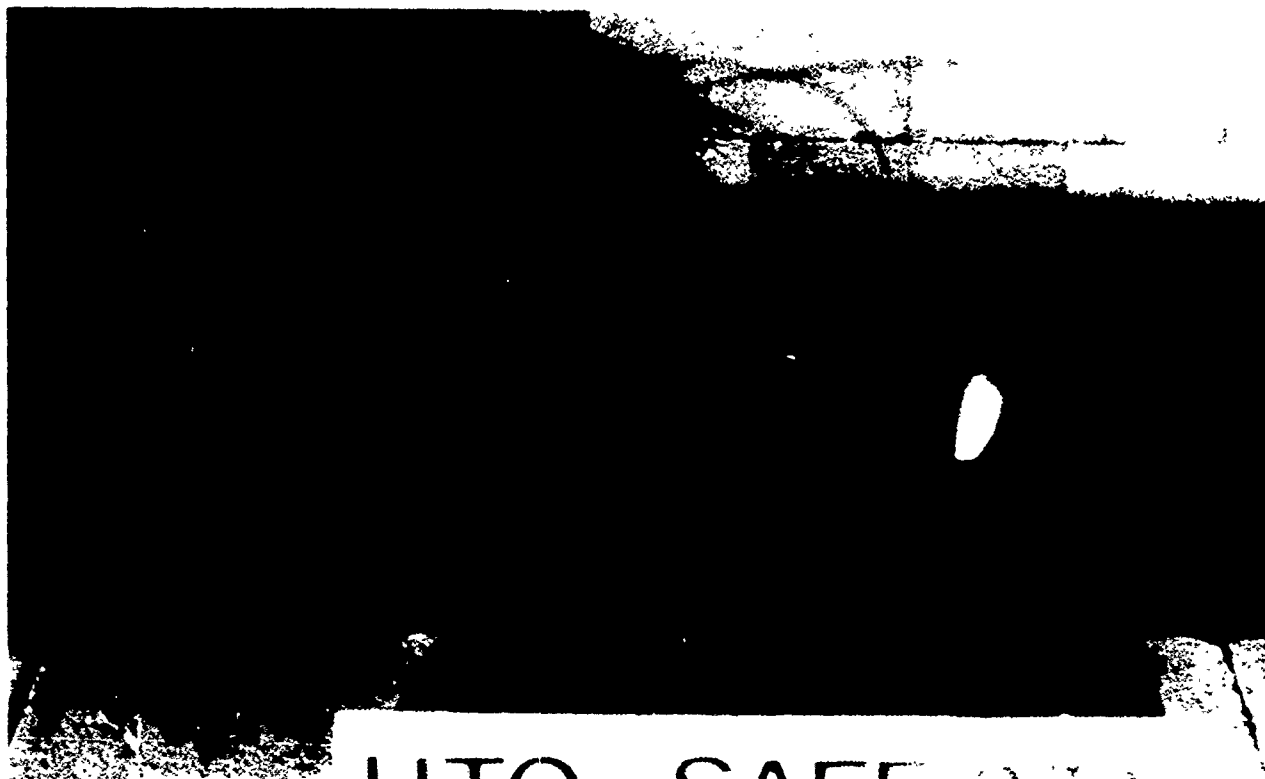


Fig. 2 Mist flammability behavior of invert emulsions (Mobil Pyrogard D) at 12,000 rpm disk speed and 850 ml/min flow rate.



HTO SAFE 273

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Fig. 3 Mist flammability behavior of water-glycol solution HTO Safe 273 at 12,000 rpm disk speed and 850 ml/min flow rate.

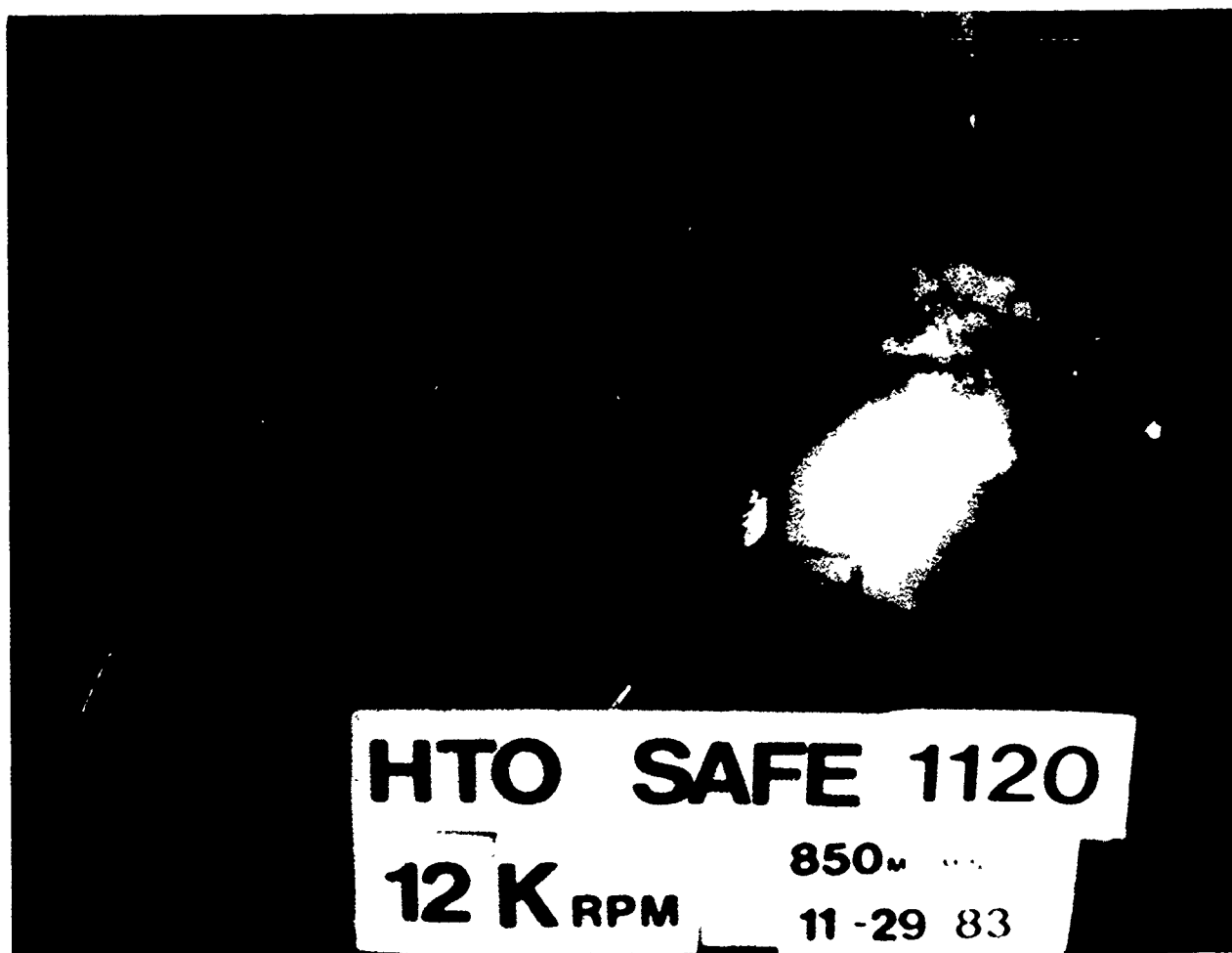


Fig. 4 Mist flammability behavior of phosphate ester HTO Safe 1120 at 12,000 rpm disk speed and 850 ml/min flow rate.

No difference was noted between the behavior of the Houghto-Safe 5046 emulsion when it was examined at the 0.5 inch burner position and at the 1.75 inch level. Except for the problem of extinguishment of the test flame by the Houghto-Safe 1120 phosphate ester at the 1.75 inch burner level, there was no significant difference between the behavior of this fluid at this level and at the 2.75 inch level.

3.1.2 2190-TEP Hydraulic Oil

The susceptibility of the 2190-TEP hydraulic oil to ignition in the flammability apparatus was amply demonstrated when the oil was tested under identically severe conditions position, imposed on the fire-resistant fluids (Table III). Thus at 0.5 inch burner position, 850 ml/min fluid delivery and at an initial disk speed of 12,000 rpm, 2190-TEP exhibited gross ignition with propagation of the resultant flame varying from $\sim 180^\circ$ to 360° around the spinning disk (Figures 5 and 6). Much variation in the degree of propagation ($\sim 90^\circ$ to 360°) was also observed among the several trials at the lower fluid delivery rate of 400 ml/min (Figures 7 and 8). High mist flammability was also observed at a much lower spray disk speed of 9500 rpm at a fluid flow rate of 850 ml/min (Figure 9). However, the typical degree of propagation around the spinning disk was 90° at a fluid flow rate of 400 ml/min, and 180° at a fluid flow rate of 850 ml/min. It is obvious from the data in Table III that as the fluid flow rate and/or initial disk speed was reduced, flame propagation was reduced. The same trend can be seen at the lower burner positions, but the magnitude of propagation was considerably less, particularly at the lowest burner level.

During testing of the 2190-TEP hydraulic oil, the photocell responded readily in contrast to the lack of significant response during screening of the fire-resistant hydraulic fluids. Table IV shows the maximum photocell output obtained over a wide range of

Table III - Mist Flammability of 2190-TEP Hydraulic Oil

| Burner Position* (Inch) | Fluid Delivery Rate, ml/min | Initial Disk Speed, rpm | Ignition | Average Circular Flame Propagation |
|-------------------------|-----------------------------|-------------------------|----------|------------------------------------|
| 0.5 | 850 | 12,000 | Yes | 180° - 360° |
| " | " | 11,000 | Yes | ~180° |
| " | " | 10,000 | Yes | ~90° |
| " | 400 | 12,000 | Yes | ~120° |
| " | " | 11,000 | Yes | ~80° |
| 1.75 | 850 | 12,000 | Yes | ~60° |
| " | " | 11,000 | Yes | ~30° |
| " | " | 10,000 | Yes | ~20° |
| " | 400 | 12,000 | Yes | ~10° |
| " | " | 11,000 | No | None |
| 2.75 | 850 | 12,000 | Yes | ~30° |
| " | " | 11,000 | Yes | ~10° |
| " | 400 | 12,000 | ** | ** |
| " | " | 11,000 | Yes | ~5° |
| " | " | 10,000 | Yes | ~5° |

* Below top of spinning disk.

** Marginal ignition.



Fig. 5 Typical mist flammability behavior of 2190 TEP (petroleum-type hydraulic fluid) showing flame propagation of $\sim 180^\circ$ at 12,000 rpm disk speed and 850 ml/min flow rate.

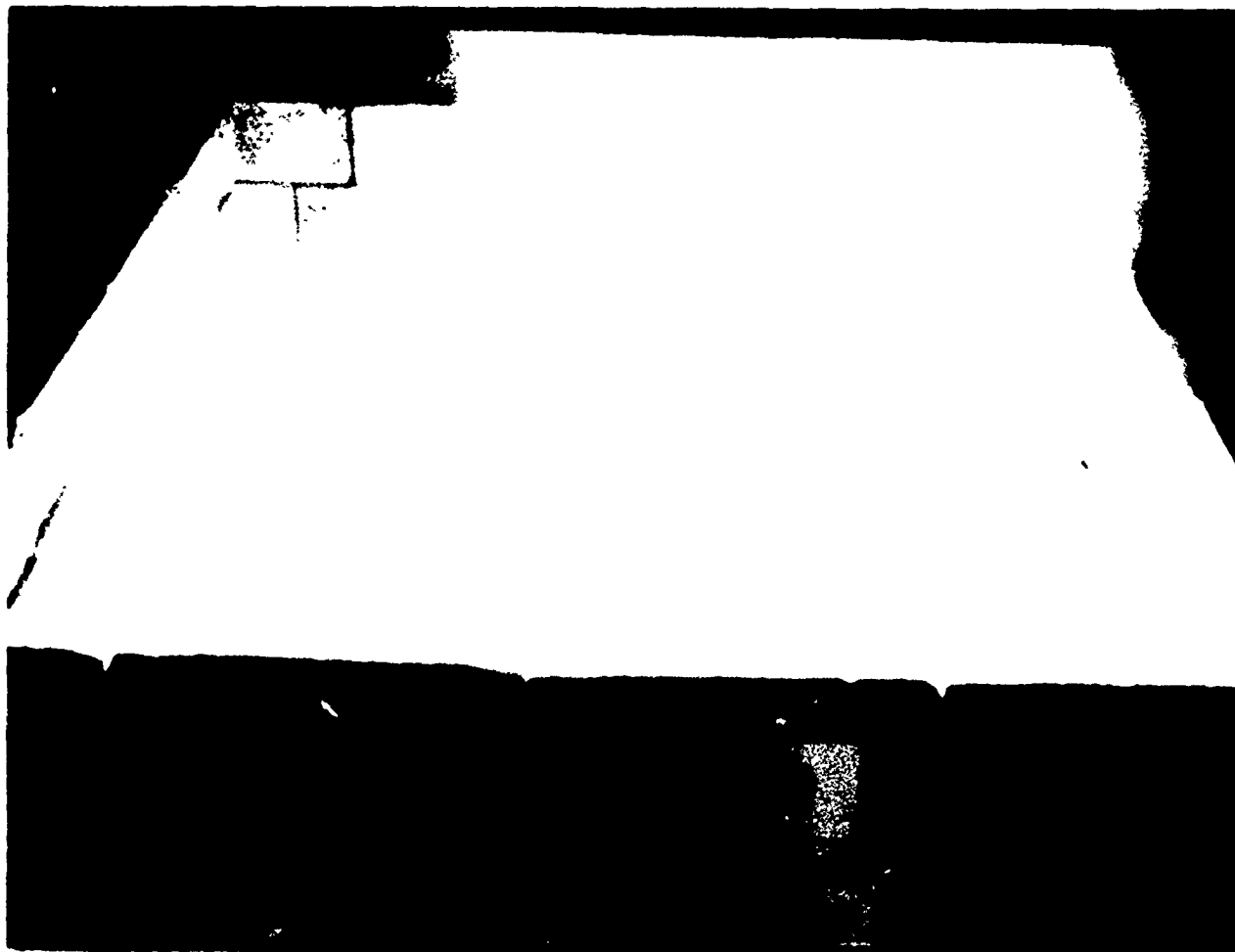


Fig. 6 Gross mist flammability of 2190 TEP showing flame propagation of 360° at 12,000 rpm disk speed and 850 ml/min flow rate.

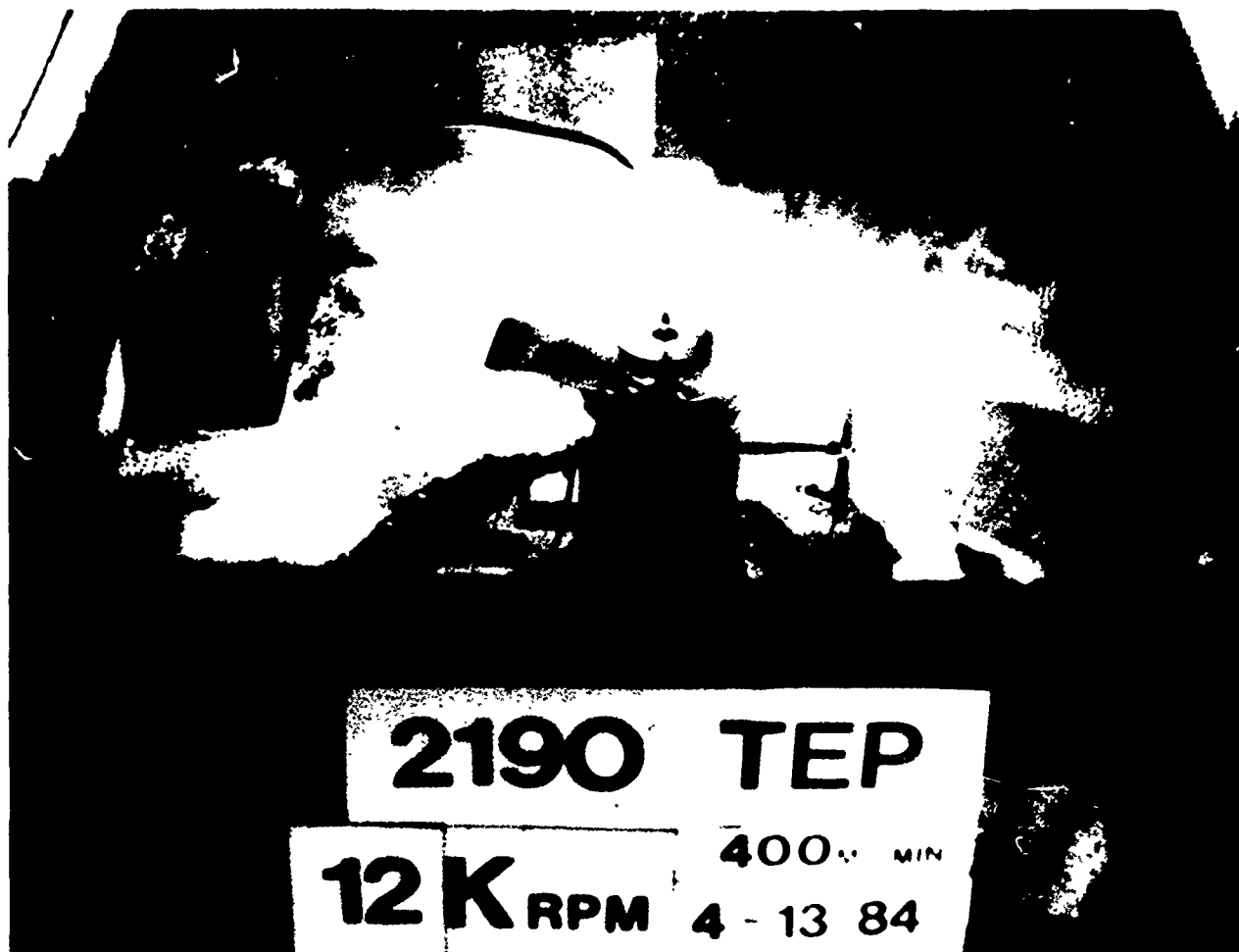


Fig. 7 Typical mist flammability behavior of 2190 TEP showing flame propagation of $\sim 90^\circ$ at 12,000 rpm disk speed and lower flow rate: 400 ml/min.



Fig. 8 Gross mist flammability of 2190 TEP showing flame propagation of 360° at 12,000 rpm disk speed and lower flow rate: 400 ml/min.



Fig. 9 Gross mist flammability of 2190 TEP showing flame propagation of 360° at lower disk speed: 9.5K and 850 m./min flow rate.

Table IV - Mist Flammability of 2190-TEP Hydraulic Oil -
Maximum Photocell Output at Decreasing Disk Speeds.

| Initial Disk Speed (rpm \pm 1%) | Tangential Disk Velocity (m/s) | Maximum Photocell Output* (millivolts) at Fluid Delivery Rate, ml/min: | |
|---|--------------------------------------|--|------|
| | | 850 | 400 |
| 12,000 | 67.8 | 19.9 | 17.7 |
| 11,500 | 65.0 | 14.5 | 16.8 |
| 11,000 | 62.2 | 19.9 | 17.2 |
| 10,500 | 59.4 | 16.3 | 15.6 |
| 10,000 | 56.6 | 19.6 | 5.5 |
| 9,500 | 53.7 | 18.2 | 7.7 |
| 9,000 | 50.9 | 18.5 | 6.2 |
| 8,500 | 48.1 | 4.2 | 7.4 |
| 8,000 | 45.2 | 1.9 | 2.8 |
| 7,500 | 42.4 | 4.1 | 3.0 |
| 7,000 | 39.6 | 1.5 | 0.6 |
| 6,500 | 36.8 | 1.3 | -- |
| 6,000 | 33.9 | 1.4 | 0.9 |

* Results obtained with burner position, 0.5 inch below top of disk.

decreasing initial disk speeds. In general, the extent of propagation decreased with decreasing disk speed (Table III). A similar reduction in photocell output might therefore be anticipated as had been observed in earlier work with jet aircraft fuels [12]. However, as seen from Table IV, there is some scatter in the data i.e., the photocell output did not decline uniformly as disk speeds were reduced, particularly when the fluid delivery was 850 ml/min. Furthermore, 2190-TEP hydraulic oil burned at times more vigorously with a variation in the amount of smoke produced; thus, the light reaching the photocell varied proportionately. The data in Table IV also show that 2190-TEP ignited in the flammability apparatus at disk speeds considerably lower than those used during the testing of the fire-resistant fluids.

3.2 DISCUSSION

The behavior of the invert emulsions in the flammability apparatus indicates that fire-resistant hydraulic fluids of this class appear promising as candidates for replacement of 2190-TEP. However, mist flammability of invert emulsions (no data given for water content) has been reported by Rowand and Sargent using a low pressure flammability test [13] based also on a spinning disk atomizer; and by Dalibert [4] (for 40% water-in-oil emulsions), using a high pressure flammability apparatus coupled with an oxyacetylene flame source. Under their test conditions, these authors [4,13] reported the invert emulsions were the most flammable of the fire-resistant fluids evaluated. This is not surprising since fire-resistancy relates to specific test conditions involving a number of factors [3c]. Differences in test results may also be related to the mist droplet size. The formation of smaller droplets in air-fluid dispersions would be more susceptible to ignition and extensive propagation of the flame. Such tests may therefore serve to differentiate the order of mist flammability among the various types of fire-resistant

hydraulic fluids and would be useful for selecting the fire-resistant hydraulic fluid according to the degree of fire-resistancy demands, providing all other requirements (viz., physical and chemical specifications) are met. In future work however, mist flammability would be better characterized as a function of the limiting mist droplet size relevant to specific hazardous conditions.

4. SUMMARY AND CONCLUSIONS

Under the severe conditions imposed on the fire-resistant hydraulic fluids evaluated in the NRL mist flammability apparatus (maximum disk speed and fluid delivery rate), all exhibited fire resistancy i.e., no ignition leading to propagation of flame from the test flame. Furthermore, no significant differences were observed in the degree of fire resistancy among the various types of fire-resistant fluids. As expected, all the fire-resistant fluids caused the test flame to become luminous as the spray passed through or contacted the flame. In contrast, the 2190-TEP petroleum type hydraulic fluid readily ignited in the flammability apparatus accompanied by circular flame propagations as large as 360°. Under much less severe conditions, ignition and flame propagation also occurred which indicated that the 2190-TEP fluid in mist form must be considered potentially hazardous.

The fire resistancy exhibited by the invert fluids under identical test conditions in the NRL flammability apparatus indicates that these materials are certainly less hazardous than the 2190-TEP hydraulic oil. Furthermore, because of their excellent physical and chemical properties, the invert emulsions hold promise as possible substitutes for 2190-TEP hydraulic oil. It is important to note that the Houghto-Safe 1120, a phosphate ester, exuded highly irritating fumes while being tested, a factor to be considered if fluids of this type are to be used in the confined space of a submarine.

Differences in results obtained with the NRL flammability apparatus and those reported by others may be due in part to difference in the spray mist droplet size obtained with each test method. In future work, mist flammability should be defined as a function of the limiting mist droplet size relevant to specific hazardous conditions.

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